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(54) **Silicone fluids and solvents thickened with silicone elastomers**

(57) Silicone gels are made by reacting an  $\equiv\text{Si-H}$  containing polysiloxane with an  $\alpha$ -olefin and an  $\alpha$ ,  $\omega$ -diene. The reaction is conducted in the presence of a platinum catalyst and a low molecular weight silicone oil or other solvent. Herein, an  $\equiv\text{Si-H}$  containing polysiloxane is grafted by long chain alkyl groups from the  $\alpha$ -olefin onto the  $\equiv\text{Si-H}$  containing

polysiloxane and then crosslinked with double bonds in the  $\alpha$ ,  $\omega$ -diene, in the presence of the low molecular weight silicone oil. The formed silicone gel is then crumbled into a silicone powder by application of mechanical force. When additional amounts of low molecular weight silicone oil are added to the gel and the silicone oil and the gel are subjected to shear force, a silicone paste is conveniently formed.

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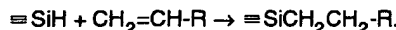
## Description

This invention provides thickened silicone oils in the form of silicone elastomers swollen into silicone gels, silicone pastes or silicone powders.

Cross-links are junctions of polymer strands in a three-dimensional network. They may be viewed as long-chain branches which are so numerous that a continuous insoluble network or gel is formed.

Increasingly, platinum catalyzed hydrosilylation reactions are being used to form networks. They typically involve reactions between a low molecular weight polysiloxane containing several  $\equiv\text{Si-H}$  groups and a high molecular weight polysiloxane containing several  $\equiv\text{Si-vinyl}$  groups or vice versa.

Attractive features of this mechanism are that (i) no by-products are formed, (ii) cross-linking sites and hence network architecture can be narrowly defined, and (iii) hydrosilylation will proceed even at room temperature to form networks. In the mechanism, crosslinking involves addition of  $\equiv\text{SiH}$  across double bonds, i.e.,



We have utilized this mechanism, but by employing some unobvious and unique modifications of the mechanism, we have formulated a new range of products having new and unique properties or ranges of application.

Our invention relates to methods of thickening silicone oils or other solvents to gel-like consistency by reacting (A) a first  $\equiv\text{Si-H}$  containing polysiloxane of the formula  $\text{R}_3\text{SiO}(\text{R}'_2\text{SiO})_a(\text{R}'\text{HSiO})_b\text{SiR}_3$  and optionally a second  $\equiv\text{Si-H}$  containing polysiloxane of the formula  $\text{HR}_2\text{SiO}(\text{R}'_2\text{SiO})_c\text{SiR}_2\text{H}$  or the formula  $\text{HR}_2\text{SiO}(\text{R}'_2\text{SiO})_a(\text{R}'\text{HSiO})_b\text{SiR}_2\text{H}$  where R, R' and R' ' are alkyl groups with 1-6 carbon atoms; a is 0-250; b is 1-250 and c is 0-250; (B) an alpha-olefin of the formula  $\text{CH}_2=\text{CR}'''\text{R}''''$  where R' ' ' is hydrogen atom or an alkyl group containing 1-40 carbon atoms and R' ' ' ' is an alkyl group containing 1-40 carbon atoms; and (C) an alpha, omega-diene of the formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_x\text{CH}=\text{CH}_2$  where x is 1-20. This reaction is conducted in the presence of a platinum catalyst and in the presence of (D) a solvent selected from organic compounds, compounds containing a silicon atom and mixtures thereof. Preferably the solvent (D) is a low molecular weight silicone oil or other solvent.

The low molecular weight silicone oil is preferably a volatile oil, although non-volatile oils can also be used. The reaction is conducted by first grafting long chain alkyl groups from the alpha-olefin onto the  $\equiv\text{Si-H}$  containing polysiloxane and then crosslinking and addition of  $\equiv\text{Si-H}$  in the grafted  $\equiv\text{Si-H}$  containing polysiloxane across double bonds in the alpha, omega-diene, until a gel is formed.

Thereafter, we crumble the silicone gel into a silicone powder using mechanical force.

Subsequently, we add additional low molecular weight silicone oil to the crumbled gel and subject the oil and gel to shear force, until a silicone paste is formed.

Silicone elastomers are prepared herein by grafting and crosslinking reaction between (A) an  $\equiv\text{Si-H}$  containing polysiloxane, (B) an alpha-olefin, (C) an alpha, omega-diene, in the presence of a platinum catalyst and (D) a low molecular weight linear or cyclic silicone oil. The resulting elastomers are then swollen with additional low molecular weight silicone oil under a shear force. Elastomers containing 65-98 weight percent of the low molecular weight silicone oil are stable and form uniform silicone pastes with a wide viscosity range.

The consequent silicone pastes have excellent properties including clarity, thixotropy, shear thinning and spread smoothly on the skin. They are applied in cosmetic and medical products as a base oil. The silicone elastomers are capable of being crumbled to form a silicone powder. This powder then has the unique property of being easily rubbed-in on the skin and silicone resins can be incorporated therein to improve the substantivity of formulations applied to the skin. These materials are ideal for use in solid cosmetics such as antiperspirants and deodorants.

The  $\equiv\text{Si-H}$  containing polysiloxane (A) is represented by compounds of the formula  $\text{R}_3\text{SiO}(\text{R}'_2\text{SiO})_a(\text{R}'\text{HSiO})_b\text{SiR}_3$ , designated herein as type A<sup>1</sup> and compounds of the formula  $\text{HR}_2\text{SiO}(\text{R}'_2\text{SiO})_c\text{SiR}_2\text{H}$  or formula  $\text{HR}_2\text{SiO}(\text{R}'_2\text{SiO})_a(\text{R}'\text{HSiO})_b\text{SiR}_2\text{H}$ , designated herein as type A<sup>2</sup>. In these formulas, R, R' and R' ' are alkyl groups with 1-6 carbon atoms; a is 0-250; b is 1-250; and c is 0-250. The molar ratio of compounds A<sup>2</sup>:A<sup>1</sup> is 0-20, preferably 0-5. In our most preferred embodiment, compounds of types A<sup>1</sup> and A<sup>2</sup> are used in the reaction, however, it is also possible to successfully conduct the reaction using only compounds of type A<sup>1</sup>.

The alpha-olefin (B) is a compound of the formula  $\text{CH}_2=\text{CR}'''\text{R}''''$ , where R' ' ' is hydrogen atom or an alkyl group containing 1-40 carbon atoms and R' ' ' ' is an alkyl group containing 1-40 carbon atoms. Representative examples of suitable alpha-olefins for use herein are propene, 1-butene, isobutylene (2-methylpropene), 1-pentene (C5), 2-methyl-1-butene, 3-methyl-1-butene, 1-hexene, 2-methyl-1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-heptene, 2-methyl-1-hexene, 1-octene, 2-methyl-1-heptene, 1-nonen, 1-decene (C10), 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene (C15), 1-hexadecene, 1-octadecene, 1-nonadecene, 1-icosene (C20), 1-heptacosene and alpha-olefin fractions containing various amounts of C<sub>22</sub>-C<sub>30+</sub> alpha-olefins sold under the trademark GULFTENE® 24-28 and GULFTENE® 30+ by the Chevron Chemical Company, Houston, Texas.

The alpha, omega-diene (C) is a compound of the formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_x\text{CH}=\text{CH}_2$  where x is 1-20. Suitable examples are 1,4-pentadiene; 1,5-hexadiene; 1,6-heptadiene; 1,7-octadiene; 1,8-nonadiene; 1,9-decadiene; 1,11-dodecadiene; 1,13-tridecadiene; and 1,19-eicosadiene.

Our grafting, addition and crosslinking reactions require a catalyst to effect the reaction between the  $\equiv\text{SiH}$  containing polysiloxane, the alpha-olefin and the alpha, omega-diene. Suitable catalysts are Group VIII transition metals, i.e., the noble metals. Such catalysts are described in US Patent 3,923,705 which shows platinum catalysts. One preferred platinum catalyst is Karstedt's catalyst, that is more fully described in US Patents 3,715,334 and 3,814,730. Karstedt's catalyst is a platinum divinyl tetramethyl disiloxane complex typically containing one weight percent of platinum in a solvent such as toluene. Another preferred platinum catalyst is a reaction product of chloroplatinic acid and an organosilicon compound containing terminal aliphatic unsaturation. This latter catalyst is more completely described in US Patent 3,419,593. The noble metal catalysts are used in amounts from 0.00001-0.5 parts, preferably 0.00001-0.02 parts, most preferably 0.00001-0.002 parts, per 100 weight parts of the  $\equiv\text{SiH}$  containing polysiloxane.

The phrase low molecular weight silicone oil (D) includes compounds containing a silicon atom such as (i) low molecular weight linear and cyclic volatile methyl siloxanes, (ii) low molecular weight linear and cyclic volatile and non-volatile alkyl and aryl siloxanes, and (iii) low molecular weight functional linear and cyclic siloxanes. Most preferred, however, are low molecular weight linear and cyclic volatile methyl siloxanes (VMS).

VMS compounds correspond to the average unit formula  $(\text{CH}_3)_2\text{SiO}_{(4-y)/2}$  in which y has an average value of two to three. These compounds contain siloxane units joined by  $\equiv\text{Si-O-Si}\equiv$  bonds. Representative units are monofunctional "M" units  $(\text{CH}_3)_3\text{SiO}_{1/2}$  and difunctional "D" units  $(\text{CH}_3)_2\text{SiO}_{2/2}$ .

The presence of trifunctional "T" units  $\text{CH}_3\text{SiO}_{3/2}$  results in the formation of branched linear or cyclic volatile methyl siloxanes. The presence of tetrafunctional "Q" units  $\text{SiO}_{4/2}$  results in the formation of branched linear or cyclic volatile methyl siloxanes.

Linear VMS compounds have the formula  $(\text{CH}_3)_3\text{SiO}\{(\text{CH}_3)_2\text{SiO}\}_y\text{Si}(\text{CH}_3)_3$ . The value of y is 0-5. Cyclic VMS compounds have the formula  $\{(\text{CH}_3)_2\text{SiO}\}_z$ . The value of z is 3-9. Preferably, these VMS have boiling points less than 250°C. and viscosities of 0.65 to 5.0 centistokes ( $\text{mm}^2/\text{s}$ ).

Representative linear VMS are hexamethyldisiloxane (MM) with a boiling point of 100°C., viscosity of 0.65  $\text{mm}^2/\text{s}$  and formula  $\text{Me}_3\text{SiOSiMe}_3$ ; octamethyltrisiloxane (MDM) with a boiling point of 152°C., viscosity of 1.04  $\text{mm}^2/\text{s}$  and formula  $\text{Me}_3\text{SiOMe}_2\text{SiOSiMe}_3$ ; decamethyltetrasiloxane ( $\text{MD}_2\text{M}$ ) with a boiling point of 194°C., viscosity of 1.53  $\text{mm}^2/\text{s}$  and formula  $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_2\text{SiMe}_3$ ; dodecamethylpentasiloxane ( $\text{MD}_3\text{M}$ ) with a boiling point of 229°C., viscosity of 2.06  $\text{mm}^2/\text{s}$  and formula  $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_3\text{SiMe}_3$ ; tetradecamethylhexasiloxane ( $\text{MD}_4\text{M}$ ) with a boiling point of 245°C., viscosity of 2.63  $\text{mm}^2/\text{s}$  and formula  $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_4\text{SiMe}_3$ ; and hexadecamethylheptasiloxane ( $\text{MD}_5\text{M}$ ) with a boiling point of 270°C., viscosity of 3.24  $\text{mm}^2/\text{s}$  and formula  $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_5\text{SiMe}_3$ .

Representative cyclic VMS are hexamethylcyclotrisiloxane ( $\text{D}_3$ ) a solid with a boiling point of 134°C. and formula  $\{(\text{Me}_2\text{SiO})_3\}$ ; octamethylcyclotetrasiloxane ( $\text{D}_4$ ) with a boiling point of 176°C., viscosity of 2.3  $\text{mm}^2/\text{s}$  and formula  $\{(\text{Me}_2\text{SiO})_4\}$ ; decamethylcyclopentasiloxane ( $\text{D}_5$ ) with a boiling point of 210°C., viscosity of 3.87  $\text{mm}^2/\text{s}$  and formula  $\{(\text{Me}_2\text{SiO})_5\}$ ; and dodecamethylcyclohexasiloxane ( $\text{D}_6$ ) with a boiling point of 245°C., viscosity of 6.62  $\text{mm}^2/\text{s}$  and formula  $\{(\text{Me}_2\text{SiO})_6\}$ .

Representative branched VMS are heptamethyl-3-((trimethylsilyl)oxy)trisiloxane ( $\text{M}_3\text{T}$ ) with a boiling point of 192°C., viscosity of 1.57  $\text{mm}^2/\text{s}$  and formula  $\text{C}_{10}\text{H}_{30}\text{O}_3\text{Si}_4$ ; hexamethyl-3,3, bis((trimethylsilyl)oxy)trisiloxane ( $\text{M}_4\text{Q}$ ) with a boiling point of 222°C., viscosity of 2.86  $\text{mm}^2/\text{s}$  and formula  $\text{C}_{12}\text{H}_{36}\text{O}_4\text{Si}_5$ ; and pentamethyl-3-((trimethylsilyl)oxy)cyclotrisiloxane ( $\text{MD}_3$ ) with the formula  $\text{C}_8\text{H}_{24}\text{O}_4\text{Si}_4$ .

Our process also includes using low molecular weight linear and cyclic volatile and non-volatile alkyl and aryl siloxanes represented respectively by formulas  $\text{R}_3\text{SiO}(\text{R}_2\text{SiO})_y\text{SiR}_3$  and  $(\text{R}_2\text{SiO})_z$ . R is alkyl groups with 2-20 carbon atoms or aryl groups such as phenyl. The value of y is 0-80, preferably 5-20. The value of z is 3-9, preferably 4-6. These polysiloxanes have viscosities generally in the range of 1-100 centistokes ( $\text{mm}^2/\text{s}$ ). Polysiloxanes can also be used where y has a value sufficient to provide polymers with a viscosity in the range of 100-1,000 centistokes ( $\text{mm}^2/\text{sec}$ ). Typically, y is 80-375. Illustrative of such polysiloxanes are polydimethylsiloxane, polydiethylsiloxane, polymethyllethylsiloxane, polymethylphenylsiloxane and polydiphenylsiloxane.

Low molecular weight functional polysiloxanes can also be employed and are represented by the formula  $\text{R}_3\text{SiO}(\text{RQSiO})_y\text{SiR}_3$  where Q is a functional group. Examples of such polysiloxanes are acrylamide functional siloxane fluids, acrylate functional siloxane fluids, amide functional siloxane fluids, amino functional siloxane fluids, carbinol functional siloxane fluids, carboxy functional siloxane fluids, chloroalkyl functional siloxane fluids, epoxy functional siloxane fluids, glycol functional siloxane fluids, ketal functional siloxane fluids, mercapto functional siloxane fluids, methyl ester functional siloxane fluids, perfluoro functional siloxane fluids and silanol functional siloxanes.

Our invention is not limited to swelling silicone elastomers with only low molecular weight polysiloxanes. Other types of solvents can also be employed to swell the silicone elastomer. Thus, a single solvent or a mixture of solvents may be used.

By solvent, we mean (i) organic compounds, (ii) compounds containing a silicon atom as enumerated above, (iii)

mixtures of organic compounds, (iv) mixtures of compounds containing a silicon atom, or (v) mixtures of organic compounds and compounds containing a silicon atom; used on an industrial scale to dissolve, suspend or change the physical properties of other materials.

In general, the above organic compounds are aromatic hydrocarbons, aliphatic hydrocarbons, alcohols, aldehydes, ketones, amines, esters, ethers, glycols, glycol ethers, alkyl halides or aromatic halides. Representative of some common organic solvents are alcohols such as methanol, ethanol, 1-propanol, cyclohexanol, benzyl alcohol, 2-octanol, ethylene glycol, propylene glycol and glycerol; aliphatic hydrocarbons such as pentane, cyclohexane, heptane, VM&P solvent and mineral spirits; alkyl halides such as chloroform, carbon tetrachloride, perchloroethylene, ethyl chloride and chlorobenzene; aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylene; esters such as ethyl acetate, isopropyl acetate, ethyl acetoacetate, amyl acetate, isobutyl isobutyrate and benzyl acetate; ethers such as ethyl ether, n-butyl ether, tetrahydrofuran and 1,4-dioxane; glycol ethers such as ethylene glycol monomethyl ether, ethylene glycol monomethyl ether acetate, diethylene glycol monobutyl ether and propylene glycol monophenyl ether; ketones such as acetone, methyl ethyl ketone, cyclohexanone, diacetone alcohol, methyl amyl ketone and diisobutyl ketone; petroleum hydrocarbons such as mineral oil, gasoline, naphtha, kerosene, gas oil, heavy oil and crude oil; lubricating oils such as spindle oil and turbine oil; and fatty oils such as corn oil, soybean oil, olive oil, rape seed oil, cotton seed oil, sardine oil, herring oil and whale oil.

"Other" miscellaneous organic solvents can also be used, such as acetonitrile, nitromethane, dimethylformamide, propylene oxide, trioctyl phosphate, butyrolactone, furfural, pine oil, turpentine and m-cresol.

Solvent further includes volatile flavoring agents such as oil of wintergreen; peppermint oil; spearmint oil; menthol; vanilla; cinnamon oil; clove oil; bay oil; anise oil; eucalyptus oil; thyme oil; cedar leaf oil; oil of nutmeg; oil of sage; cassia oil; cocoa; licorice; high fructose corn syrup; citrus oils such as lemon, orange, lime and grapefruit; fruit essences such as apple, pear, peach, grape, strawberry, raspberry, cherry, plum, pineapple and apricot; and other useful flavoring agents including aldehydes and esters such as cinnamyl acetate, cinnamaldehyde, eugenyl formate, p-methylanisole, acetaldehyde, benzaldehyde, anisic aldehyde, citral, neral, decanal, vanillin, tolyl aldehyde, 2,6-dimethyloctanal and 2-ethyl butyraldehyde.

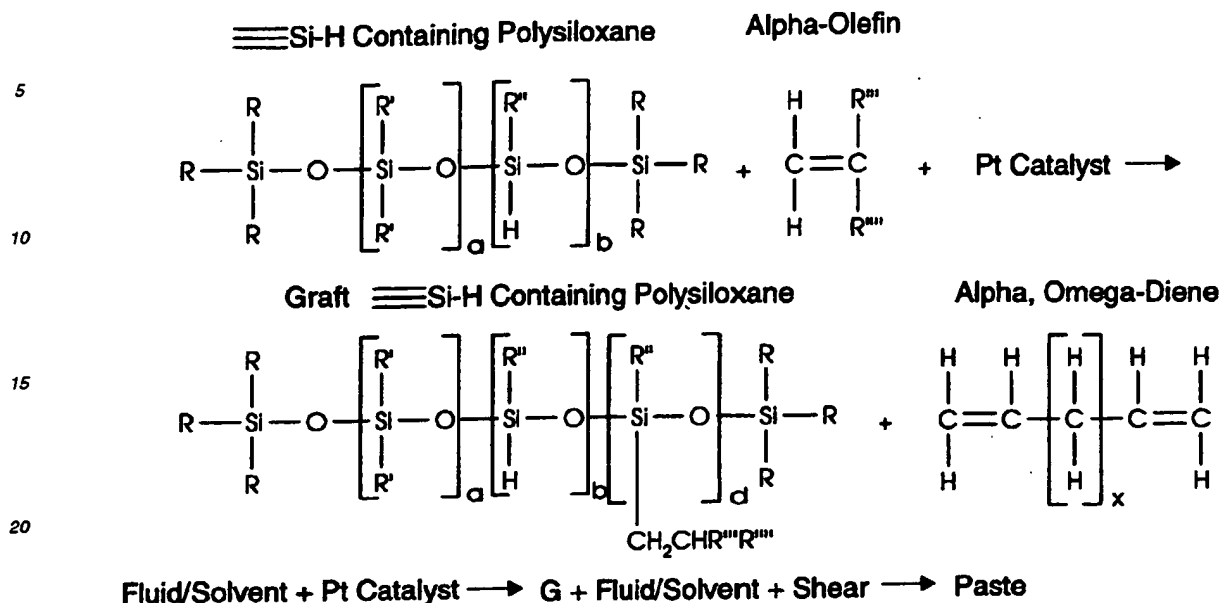
In addition, solvent includes volatile fragrances such as natural products and perfume oils. Some representative natural products and perfume oils are ambergris, benzoin, civet, clove, leaf oil, jasmine, mate, mimosa, musk, myrrh, orris, sandalwood oil and vetiver oil; aroma chemicals such as amyl salicylate, amyl cinnamic aldehyde, benzyl acetate, citronellol, coumarin, geraniol, isobornyl acetate, ambrette and terpinyl acetate; and the various classic family perfume oils such as the floral bouquet family, the oriental family, the chypre family, the woody family, the citrus family, the canoe family, the leather family, the spice family and the herbal family.

Execution of our process is simply a matter of combining the  $\equiv\text{SiH}$  containing polysiloxane(s), the alpha-olefin, the alpha, omega-diene, the low molecular weight silicone oil or other solvent and the catalyst; and then mixing these ingredients at room temperature until a gel is formed. Higher temperatures to speed up the process can be used, if desired.

Additional amounts of the low molecular weight silicone oil or solvent are then added to the gel and the resulting mixture is subjected to shear force to form a paste. Any type of mixing and shearing equipment may be used to perform these steps such as a batch mixer, planetary mixer, single or multiple screw extruder, dynamic or static mixer, colloid mill, homogenizer, sonolator or a combination thereof.

Typically, we carry out the process using approximately a 1:1 molar ratio of  $\equiv\text{Si-H}$  containing polysiloxane to vinyl groups from the alpha-olefin and the alpha, omega-diene. It is expected that useful materials may also be prepared by carrying out the process with an excess of the  $\equiv\text{Si-H}$  containing polysiloxane or the vinyl containing compounds, but this would be considered a less efficient use of the materials. The remainder of the composition comprises the low molecular weight silicone oil or other solvent in amounts generally within the range of 65-98 percent by weight of the composition, preferably 80-98 percent by weight.

Most preferably, however, the low molecular weight silicone oil is thickened by the silicone elastomers in a two-step process. In the first step, the  $\equiv\text{SiH}$  containing polysiloxane is grafted with long alkyl groups by contacting it with the alpha-olefin in the presence of the platinum catalyst. In the second step, the  $\equiv\text{SiH}$  containing polysiloxane grafted with long alkyl groups from the alpha-olefin is crosslinked by contact with the alpha, omega-diene, in the presence of the low molecular weight silicone oil and platinum catalyst. An elastomer with a more hydrocarbon character is thereby produced, compared to elastomers made by using only an alpha, omega-diene. A representation of this two-step process is shown below:



Alternatively, thickening with silicone elastomers herein is performed in one-step by gelation of a mixture including the  $\equiv\text{SiH}$  containing polysiloxane, the alpha-olefin, the alpha, omega-diene, the low molecular weight silicone oil and the platinum catalyst. Silicone elastomers made in one- or two-steps are equally capable of being swollen with the low molecular weight silicone oil under shear force and both processes provide uniform silicone pastes. While these silicone pastes have excellent spreadability upon rubbing and possess unique rheological properties in being thixotropic and shear thinning, they also possess the added benefit of being more compatible with hydrophobic materials such as mineral oil.

The following examples are set forth to further illustrate our invention in more detail.

#### Example 1

100 grams of an organopolysiloxane with the average structure  $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_{60}(\text{MeHSiO})_8\text{SiMe}_3$ , where Me is, and hereafter, represents methyl and 17.55 grams of an alpha-olefin with the average structure  $\text{CH}_2=\text{CH}(\text{CH}_2)_{24}\text{CH}_3$  were mixed in a flask. To this solution was added 20  $\mu\text{l}$  of Karstedt's catalyst containing two weight percent of platinum in a two centistoke ( $\text{mm}^2/\text{s}$ ) polydimethylsiloxane fluid. This solution was stirred for 3 hours. The resulting product (14 grams) and alpha, omega-diene 1,5-hexadiene (0.542 gram) were then mixed with 66 grams of decamethylcyclopentasiloxane ( $\text{D}_5$ ) in a reaction vessel. 20  $\mu\text{l}$  of Karstedt's catalyst was again added while the solution was stirred. Gelation occurred within one hour. The gel was left in the reaction flask overnight and then 60 parts by weight of the gel were swollen with 46 parts by weight of decamethylcyclopentasiloxane under a shear force. A uniform paste was obtained having a viscosity of  $1.08 \times 10^6$  centipoise ( $\text{mPa}\cdot\text{s}$ ) at a shear rate of 0.025 reciprocal seconds ( $\text{s}^{-1}$ ). The paste was next mixed with mineral oil and found to be compatible with mineral oil in any weight ratio. This example illustrates our two-step method.

#### Example 2

25 grams of an organopolysiloxane with the average structure  $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_{16}(\text{MeHSiO})_{39}\text{SiMe}_3$  and 49 grams of alpha-olefin  $\text{CH}_2=\text{CH}(\text{CH}_2)_{15}\text{CH}_3$  were mixed in a flask. To this solution was added 20  $\mu\text{l}$  of Karstedt's catalyst and the solution was stirred for one hour. This product (3 grams), 5 grams of an organopolysiloxane with the average structure  $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_{93}(\text{MeHSiO})_6\text{SiMe}_3$  and 1,5-hexadiene (0.285 gram) were mixed with 37 grams of decamethylcyclopentasiloxane in a reaction vessel. 20  $\mu\text{l}$  of Karstedt's catalyst was again added while the solution was stirred. Gelation took place within a few hours. The gel was placed in an  $80^\circ\text{C}$ . oven for three hours and then 43 parts by weight of the gel were swollen with 34 parts by weight of decamethylcyclopentasiloxane under a shear force. A uniform paste was obtained with a viscosity of  $5.77 \times 10^5$  centipoise ( $\text{mPa}\cdot\text{s}$ ) at a shear rate of  $0.025 \text{ s}^{-1}$ . The paste was mixed with mineral oil and found to be compatible with mineral oil in any weight ratio. This example also illustrates

our two-step method.

#### Example 3

In a reaction vessel, 15 grams of an organopolysiloxane with the average structure  $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_{60}(\text{MeH-SiO})_8\text{SiMe}_3$ , 1.24 grams of alpha-olefin  $\text{CH}_2=\text{CH}(\text{CH}_2)_{15}\text{CH}_3$ , 0.73 gram of alpha, omega-diene 1,5-hexadiene and 68 grams of decamethylcyclopenta-siloxane were mixed together. To this solution was added 20  $\mu\text{l}$  of Karstedt's catalyst. The solution was stirred until it gelled. The gel was placed in an 80°C. oven for four hours and then 50 parts by weight of the gel were swollen with 50 parts by weight of decamethylcyclopentasiloxane under a shear force. A uniform paste was obtained with a viscosity of  $1.9 \times 10^6$  centipoise (mPa·s) at a shear rate of  $0.025 \text{ s}^{-1}$ . The paste was mixed with mineral oil and found to be compatible with mineral oil in any weight ratio. This example illustrates our one-step method.

#### Example 4 - Comparison Example

A gel was made from 12 grams of an organopolysiloxane with the average structure  $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_{93}(\text{MeH-SiO})_6\text{SiMe}_3$ , 0.412 gram of alpha, omega-diene 1,5-hexadiene, 80.7 grams of decamethylcyclopenta-siloxane and 20  $\mu\text{l}$  of Karstedt's catalyst. Sixty grams of this gel were swollen with 34 grams of decamethylcyclopenta-siloxane under a shear force. A paste was obtained and mixed with mineral oil. The paste and mineral oil had poor compatibility. This was evidenced by the development of haziness and the eventual phase separation which occurred.

Silicone pastes prepared according to Examples 1-3 are compatible with emollient oils other than mineral oil, such as peanut oil, sesame oil, avocado oil, coconut oil, cocoa butter, almond oil, safflower oil, corn oil, cotton seed oil, castor oil, olive oil, jojoba oil, paraffin oil, cod liver oil, palm oil, soybean oil, wheat germ oil, linseed oil and sunflower seed oil; fatty acid esters such as isopropyl myristate, isopropyl palmitate, octyl palmitate, isopropyl stearate, butyl stearate, cetyl stearate, diisopropyl adipate, isodecyl oleate, diisopropyl sebacate and lauryl lactate; fatty acids such as lauric, myristic, palmitic, stearic, oleic, linoleic and behenic acid; fatty alcohols such as lauryl, myristyl, cetyl, stearyl, isostearyl, oleyl, ricinoleyl, erucyl and 2-octyl dodecanol, alcohol; lanolin and its derivatives such as lanolin, lanolin oil, lanolin wax, lanolin alcohols, lanolin fatty acids, isopropyl lanolate, ethoxylated lanolin and acetylated lanolin alcohols such as ACETULAN®, a trademark and product of Amerchol Corporation, Edison, New Jersey; hydrocarbons such as petrolatum and squalane; and mixtures of branched chain hydrocarbons sold under the tradename ISOPAR by the Exxon Chemical Company, Houston, Texas.

The silicone elastomer, silicone gel, silicone paste and silicone powder compositions of our invention have particular value in the personal care arena. Because of the unique volatility characteristics of the VMS component of these compositions, they can be used alone or blended with other cosmetic fluids, to form a variety of over-the-counter (OTC) personal care products.

Thus, they are useful as carriers in antiperspirants and deodorants, since they leave a dry feel and do not cool the skin upon evaporation. They are lubricious and will improve the properties of skin creams, skin care lotions, moisturizers, facial treatments such as acne or wrinkle removers, personal and facial cleansers, bath oils, perfumes, colognes, sachets, sunscreens, pre-shave and after-shave lotions, liquid soaps, shaving soaps and shaving lathers. They can be used in hair shampoos, hair conditioners, hair sprays, mousses, permanents, depilatories and cuticle coats, to enhance gloss and drying time and provide conditioning benefits.

In cosmetics, they will function as leveling and spreading agents for pigments in make-ups, color cosmetics, foundations, blushes, lipsticks, lip balms, eyeliners, mascaras, oil removers, color cosmetic removers and powders. They are useful as delivery systems for oil and water soluble substances such as vitamins. When incorporated into sticks, gels, lotions, aerosols and roll-ons, the compositions impart a dry, silky-smooth, payout.

In addition, the compositions exhibit a variety of advantageous and beneficial properties such as clarity, shelf stability and ease of preparation. Hence, they have wide application, but especially in antiperspirants, deodorants, in perfumes as a carrier and for conditioning hair.

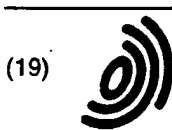
Our silicone elastomers, gels, pastes and powders also have uses beyond the personal care arena, including their use as a filler or insulation material for electrical cable, a soil or water barrier for in-ground stabilization or as a replacement for epoxy materials used in coil-on-plug designs in the electronics industry.

They are further useful as a carrier for crosslinked silicone rubber particles. In that application, (i) they allow ease of incorporation of the particles into such silicone or organic phases as sealants, paints, coatings, greases, adhesives, antifoams and potting compounds; and (ii) they provide for modifying rheological, physical or energy absorbing properties of such phases in either their neat or finished condition.

In addition, our silicone elastomers, gels, pastes and powders, are capable of functioning as carriers for pharmaceuticals, biocides, herbicides, pesticides and other biologically active substances; and can be used to incorporate water and water-soluble substances into hydrophobic systems. Examples of some water-soluble substances are salicylic acid, glycerol, enzymes and glycolic acid.

## Claim

1. A method of thickening solvents comprising reacting (A) a first  $\equiv\text{Si-H}$  containing polysiloxane of the formula  $\text{R}_3\text{SiO}(\text{R}'_2\text{SiO})_a(\text{R}'\text{HSiO})_b\text{SiR}_3$  and optionally a second  $\equiv\text{Si-H}$  containing polysiloxane of the formula  $\text{HR}_2\text{SiO}(\text{R}'_2\text{SiO})_c\text{SiR}_2\text{H}$  or the formula  $\text{HR}_2\text{SiO}(\text{R}'_2\text{SiO})_a(\text{R}'\text{HSiO})_b\text{SiR}_2\text{H}$  where R, R' and R' ' are alkyl groups of 1-6 carbon atoms; a is 0-250; b is 1-250; and c is 0-250; (B) an alpha-olefin of the formula  $\text{CH}_2=\text{CR}'''\text{R}''''$  where R' '' is hydrogen atom or an alkyl group containing 1-40 carbon atoms and R' ''' is an alkyl group containing 1-40 carbon atoms; and (C) an alpha, omega-diene of the formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_x\text{CH}=\text{CH}_2$  where x is 1-20; conducting the reaction in the presence of a platinum catalyst and (D) a solvent selected from the group consisting of (i) organic compounds, (ii) compounds containing a silicon atom, (iii) mixtures of organic compounds, (iv) mixtures of compounds containing a silicon atom, and (v) mixtures of organic compounds and compounds containing a silicon atom; and continuing the reaction until a gel is formed.
2. A method according to claim 1 including the further steps of adding additional solvent to the gel and subjecting the solvent and gel to shear forces until a paste is formed.
3. A method according to claim 1 including the further step of using mechanical force to crumble the gel until a powder is obtained.
4. A product containing the gel obtained by the method of claim 1, selected from antiperspirants, deodorants, skin creams, skin care lotions, moisturizers, acne removers, wrinkle removers, facial cleansers, bath oils, perfumes, colognes, sachets, sunscreens, pre-shave lotions, after-shave lotions, liquid soaps, shaving soaps, shaving lathers, hair shampoos, hair conditioners, hair sprays, mousses, permanents, depilatories, cuticle coats, make-ups, color cosmetics, foundations, blushes, lipsticks, lip balms, eyeliners, mascaras, oil removers, cosmetic removers, delivery systems for oil and water soluble substances and pressed powders; including such products in the form of sticks, gels, lotions, aerosols and roll-ons.
5. A product containing the gel obtained by the method of claim 1 and a material selected from crosslinked silicone rubber particles, pharmaceuticals biocides, herbicides, pesticides, water and water-soluble substances.
6. A method of modifying rheological, physical or energy absorbing properties, of silicone or organic phases selected from the group consisting of sealants, paints, coatings, greases, adhesives, antifoams and potting compounds, comprising incorporating therein the gel obtained by the method of claim 1 containing crosslinked silicone rubber particles.
7. A method of filling or insulating an electrical cable comprising incorporating therein the gel obtained by the method of claim 1.
8. A method of stabilizing in-ground soil or water barriers comprising incorporating into soil the gel obtained by the method of claim 1.
9. A method for manufacture of a personal care product comprising formulating the product of claim 4 for cosmetic use.
10. A method of improving the appearance of hair or skin which comprises topically applying thereto the product of claim 4 in an amount effective to enhance the appearance of said hair or skin.
11. Use of the product of claim 4 as a personal care product for applying to hair or skin.



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(54) **Silicone fluids and solvents thickened with silicone elastomers**

(57) Silicone gels are made by reacting an  $\equiv\text{Si-H}$  containing polysiloxane with an alpha-olefin and an alpha, omega-diene. The reaction is conducted in the presence of a platinum catalyst and a low molecular weight silicone oil or other solvent. Herein, an  $\equiv\text{Si-H}$  containing polysiloxane is grafted by long chain alkyl groups from the alpha-olefin onto the  $\equiv\text{Si-H}$  containing

polysiloxane and then crosslinked with double bonds in the alpha, omega-diene, in the presence of the low molecular weight silicone oil. The formed silicone gel is then crumbled into a silicone powder by application of mechanical force. When additional amounts of low molecular weight silicone oil are added to the gel and the silicone oil and the gel are subjected to shear force, a silicone paste is conveniently formed.

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## EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	GB 1 093 904 A (DOW) * page 1, line 69 - line 75 * * page 3, line 73 - line 78 * * example 1 *	1,7	C08G77/50 C08L83/04
Y	US 5 493 041 A (T. N. BIGGS ET AL.) 20 February 1996 * column 3, line 32 - line 40 * * claim 1 *	1-6,8-11	
Y	EP 0 501 791 A (SHIN-ETSU) 2 September 1992 * abstract * * Synthetic Example 1 * * page 4, line 50 - page 5, line 30 * * examples 2-4 * * page 8 *	1-6,8-11	
X	EP 0 298 402 A (DOW) 11 January 1989 * page 2, line 24 - line 25 * * page 3, line 48 - line 49 * * page 7, line 47 - line 54 * * example 1 * * claim 1 *	1,2	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C08G C08L
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 4 December 1998	Examiner Hoepfner, W
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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